



Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends

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ABSTRACT

The thermal behavior of plastics (PS and HDPE) and their blends with biomass (bamboo, empty fruit bunch and sawdust) was investigated in this paper. The individual devolatilization behavior of each of the fuels obtained separately was compared with the behavior of the biomass blends with plastics at various blends. The result shows that the thermal decomposition of the materials can be characterized by one single reaction stage while that of the blends can be characterized by two decomposition reaction stages. The results of the analyses suggested that the co-pyrolysis characteristics of the blends are quite different to the combination of the individual materials and therefore the possible synergic effect points to the existence of chemical interactions during co-pyrolysis between the plastic and biomass fractions of the blends. While up to 25% deviation was observed between the experimental and calculated TGA for HDPE/biomass blends, up to 40% was observed for PS/biomass blends. The examination of the kinetic of the blends indicated that an increase in plastic percentage in the blends leads to decrease of activation energy for the first decomposition stage reaction and subsequently increases the activation energy for the second decomposition stage reaction.

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1. Introduction

One of the thermochemical processes used in waste treatment is the pyrolysis process. This process is preferred because of the products generated and the opportunity to recover energy. It is also a precursor for other thermochemical processes like the combustion and gasification processes. The thermal co-processing of waste mixtures otherwise known as co-pyrolysis had gained a lot of attention recently. Many experiments have been done using the thermogravimetric analysis (TGA) [1] and different pyrolysis reactors to establish the several synergic effects that can be achieved through the co-pyrolysis of different waste materials. During the pyrolysis of some feedstock, obtaining high quality and quantity of some fraction of products can be very challenging. For example, the tars obtained from biomass pyrolysis are mostly unstable and oxygenated [2], so it is very challenging to upgrade the liquid and co-pyrolyzing the feedstock with other material can be beneficial in some regards. Also biomass and coal have low hydrogen to carbon ratio and therefore gives low liquid yield. Most researchers have studied the co-pyrolysis of biomass/coal with plastics or synthetic polymers and obtained higher quantity and better quality of oil in comparison with those obtained from biomass or coal pyrolysis alone [3–8].

Plastics and synthetic polymers have high hydrogen contents and are therefore used to provide hydrogen during co-pyrolysis which can lead to increase liquid production. Vasile and Brebu [7] in their work concluded that synthetic polymers acts as hydrogen source in thermal co-processing with organic materials like coal or most biomass which have less hydrogen content. Lazaro et al. [4] also claimed that pyrolyzing coal alone will allow the transfer of coal hydrogen into molecular hydrogen instead of forming liquid and therefore it is necessary to supply more hydrogen from other sources to improve the coal pyrolysis behavior. In literature, most emphasis is on the improvement of the liquid fraction but also co-pyrolysis tends to enhanced the quality of other fractions especially char. Co-pyrolysis chars obtained by Brebu et al. [3] had higher calorific values compared to that obtained in the pyrolysis of biomass alone and Bernardo et al. in their work on co-pyrolysis of waste mixtures also claimed that co-pyrolysis process helps to produce high quality chars [9].

Co-pyrolysis of waste mixtures or different feedstock can also help to resolve issues related to limited supply of some feedstock. For example, Lazaro et al. while studying the co-pyrolysis of coal and lube oil wastes [4] claimed that pyrolyzing lube oil wastes alone might be limited by supply which could be economically challenging due to the small size plants that would be lower than the critical size needed to have any economic benefits. Recently, Lam et al. [10] carried out the numerical study of mixed-feedstock pyrolysis and concluded that mixing feedstock during pyrolysis can increase the solid retention time and also reduce the char deposition on the reactor wall. Also in a recent work on

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co-pyrolysis [11], modeling approach was used to justify energy usage reduction during co-pyrolysis of biomass and plastic wastes.

Thermogravimetric studies suggested that biomass start to decompose at a lower temperature [12] while plastic materials decompose at a temperature range of 673–773 K depending on the specific type of plastic [13]. Thermogravimetric analysis has been used extensively over the years to investigate the thermal events and kinetics during pyrolysis of organic materials and it provides a measurement of the weight loss of a sample as a function of temperature and time. A detailed knowledge and understanding of the thermogravimetric analysis and the devolatilization kinetics will help in planning, designing and operation of the industrial pyrolysis processes [14,15]. Recently, some studies [1,3,16–18] have been carried out on co-pyrolysis characteristics of plastics and biomass blends but some of these works have only concentrated on the effect on the products of the co-pyrolysis. While others considered only one biomass and plastics material or considered only one ratio-blends during the co-pyrolysis. For example, Çepelioğullar and Pütün investigated the co-pyrolysis characteristics and kinetics of biomass-plastic blends at definite ratio of 1:1 [16], while Brebu et al. [3] only investigated the effect of co-pyrolysis on the products yields and quality of pyrolysis oil and chars. In order to adequately understand the interaction that exists between various biomass and plastic blends, there is need to investigate the process at more blends and comparing the behavior of different biomass in the mixtures.

Therefore, this study provides comprehensive experimental data on the effect of plastic blending on the co-pyrolysis behavior of biomass. The specific objectives include the investigation and comparison of thermal and decomposition behaviors of plastic/biomass mixtures, the kinetic analysis and the discussion on the synergic effects by detailed comparison of the experimental and calculated TGA analysis. Three different biomass materials (pine wood sawdust, bamboo and empty fruit bunch) were blended at four different definite ratios of 1:4, 2:3, 3:2 and 4:1 w/w with two different plastic materials (high density polyethylene and polystyrene). Thermogravimetric analyzer was used for the co-pyrolysis process to obtain an overall understanding of the interaction of plastics and biomass wastes. The kinetic data were obtained and the co-pyrolysis and kinetics of the blends are then explained in details.

2. Methodology

2.1. Sample preparation

High density polyethylene (HDPE) and polystyrene (PS) are the two major plastic type considered in this work. HDPE is one of the most common plastic wastes and PS is also selected due to its difference in composition to HDPE. The samples were obtained as analytical grade from major suppliers. The materials are blended and further reduced to mesh size less than 0.08 mm using an ultra-centrifugal mill Retsch® ZM200. The biomass used for this work are pine wood sawdust, bamboo and empty fruit bunch (EFB). The pine wood sawdust was obtained from a local sawmill in Hong Kong, while the bamboo sample was obtained from a construction site inside the campus of Hong Kong University of Science and Technology. The empty fruit Bunch (EFB) was obtained from a research group at University of Nottingham, Malaysia. The biomass were cut into small chips and further blended into smaller sizes. The samples were then dried in an oven at 378 K for 48 h. The dried biomass samples were then further reduced to mesh size less than 0.08 mm using the ultra-centrifugal mill Retsch® ZM200 for TGA purpose. From these materials, four biomass – plastic blends were prepared with weight percentages of 20%, 40%, 60% and 80%.

2.2. Experimental analysis

The samples were analyzed to determine the main parameters. The calorific value of the samples was measured using a Parr 6100 bomb calorimeter. The proximate analysis determination was made according

to the standard practice for Proximate Analysis of Coal and Coke (ASTM D5142-09).

The pyrolysis characteristics of the samples and blends were examined using a thermogravimetric analyzer (TGA/DSC 1, Mettler Toledo – Star^e System). A 150 mL Al₂O₃ crucible was loaded with about 10 mg sample and subjected to a heating rate of 10 K/min from room temperature to 1073 K using a nitrogen flow rate of 50 mL/min. Once the sample temperature reached 383 K, the pyrolysis was held in an isothermal condition for 5 min to completely remove the moisture and provide a basis for analysis. The experiment was carried out at least twice for each sample and the reproducibility was good with deviations mainly occurring at temperatures below the reaction range and below 1%.

2.3. Kinetics method

Generally the rate of non-isothermal solid decomposition can be described by Eq. (1).

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where α is the conversion of the combustible material and it is defined as

$$\alpha = \frac{m_i - m}{m_i - m_f} \quad (2)$$

where m , m_i and m_f represent the instantaneous, initial (at 383 K) and final mass of the sample. The reaction rate constant k is expressed in terms of the Arrhenius equation as

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

The function $f(\alpha)$ can be written as;

$$f(\alpha) = (1-\alpha)^n \quad (4)$$

Substituting into Eq. (1) gives

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) (1-\alpha)^n \quad (5)$$

Considering a constant heating rate $\beta = dT/dt$, Eq. (5) can be rearranged to the following equation.

$$\frac{d\alpha}{dT} = \left(\frac{1}{\beta}\right) A \exp\left(\frac{-E}{RT}\right) (1-\alpha)^n \quad (6)$$

Eq. (6) was integrated using the integral method based on Coats and Redfern equation which was also used recently by [19,20] and the approximation is given as

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad \text{if } n = 1 \quad (7)$$

or

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{(1-n) \times T^2} \right] = \ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad \text{if } n \neq 1 \quad (8)$$

In most cases, $2RT/E$ is very small and therefore the two equations can be approximated by;

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad \text{if } n = 1 \quad (9)$$

Table 1
Proximate and ultimate analyses (wt.%) of the samples.

Sample	Proximate analysis				Ultimate analysis (daf)				$S_{t,d}$	H/C	O/C	GCV (MJ/kg)
	M_{ad}	A_d	VM_{daf}	FC_{daf}	C	H	N	O_{diff}				
Bamboo	6.14	1.95	83.95	16.05	50.52	6.04	0.58	>42.80	0.09	1.4247	0.6356	17.87
Sawdust	10.81	2.58	83.12	16.88	44.19	6.03	2.47	>46.80	0.54	1.6263	0.7947	16.63
EFB	8.43	3.50	83.52	16.48	48.93	6.12	1.04	>43.30	0.61	1.4895	0.6641	16.77
HDPE	0.28	0.56	99.69	0.31	85.65	13.20		>0.87	0.28	1.8381	0.0076	44.04
PS	0.29	0.09	99.96	0.04	92.12	7.88		>0.01		1.0194		41.29

diff: by difference; M_{ad} : moisture (air dried base); A_d : ash (moisture-free base); VM_{daf} : volatile matter (dried and ash-free base); FC_{daf} : fixed carbon (dried and ash-free base); $S_{t,d}$: total sulfur (dry base).

or

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n) \times T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad \text{if } n \neq 1 \quad (10)$$

The plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$ becomes a linear line for $n = 1$; the plot of $\ln[1 - (1 - \alpha)^{(1-n)/(1-n) \times T^2}]$ for $n \neq 1$. The activation energy (E) and the pre-exponential factor (A) can be determined from the slope and intercept of the regression line respectively.

3. Results and discussion

The proximate analysis, calorific values and the ultimate analysis of the samples are shown in Table 1. The plastic materials have different properties, the calorific value of HDPE was higher than that of PS, while bamboo wastes have higher calorific value than that of sawdust and EFB. The plastic material especially PS was mostly volatile and are expected to completely burn off when pyrolyzed alone. The sawdust materials have higher moisture compared to the other two biomass materials. Bamboo wastes have higher carbon content compared to the other two biomass samples and therefore lower H/C and O/C ratios due to the low hydrogen and oxygen content respectively.

3.1. Pyrolysis characteristics of materials

The pyrolysis processes of the materials are characterized by three-stage degradation with decomposition taking place majorly in the second stage as shown in Fig. 1. The decomposition of HDPE occurs at a temperature range of 663–768 K, while that of PS occurs at 623–713 K. The peak temperature of HDPE (733 K) was higher than that of PS (678 K) with a higher decomposition intensity of 5.936 wt.%/K compared to 2.88 wt.%/K for PS. The temperature

range for the decomposition of the biomass was wider than that of the plastic material. EFB starts decomposition lower than bamboo and sawdust, though for the decomposition of the biomass materials, the decomposition range for bamboo, sawdust and EFB occurs at 458–683 K, 448–688 K and 428–688 K respectively. Among the biomass materials, the peak temperature of bamboo was the highest at 613 K with decomposition intensity of 1.0284 wt.%/K followed by sawdust with peak temperature of 608 K and decomposition intensity of 0.8611 wt.%/K, while the peak temperature of EFB occurs at lower temperature of 563 K with decomposition intensity of 0.8047 wt.%/K.

It is important to note that during the decomposition of bamboo, there exists a peak which appears as a shoulder to the left of the main degradation peak in the DTG curve. This can be attributed to the decomposition of hemicellulose between the temperature range of 473–580 K. However, this observation was not conspicuous with sawdust and EFB.

The TGA and DTG curve revealed that for the pyrolysis of the raw sample, the mass loss could be regressed as a single step process.

3.2. Pyrolysis characteristics of co-pyrolysis blends

When plastic and biomass are mixed together, the pyrolysis is characterized by two decomposition stages unlike one decomposition stage that was observed when the materials are pyrolyzed alone. The decomposition intensity change based on the type of co-pyrolyzed mixtures and the percentage of each material in the blends.

Overall, the first decomposition stage is majorly attributed to decomposition of biomass material and slightly affected by the plastic materials since the reaction is below 643 K for all blends. As stated by Han et al. [18], plastics softens at this temperature but do not decompose and therefore can affect the heat and mass transfer processing at this range. The second decomposition stage is a combination of the thermal degradation of biomass and plastic material in the mixtures. Lignin

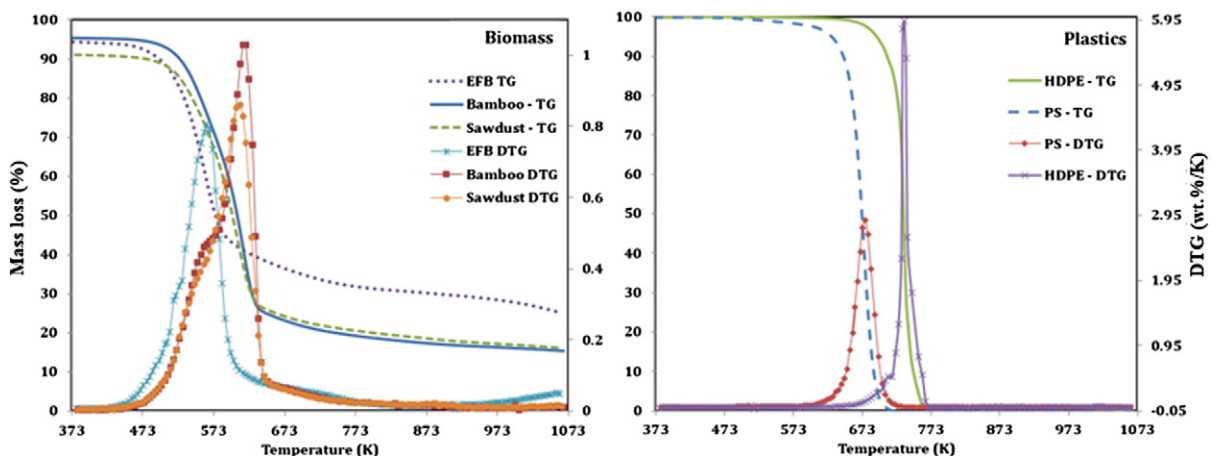


Fig. 1. Pyrolysis TG and DTG curves of plastics and biomass.

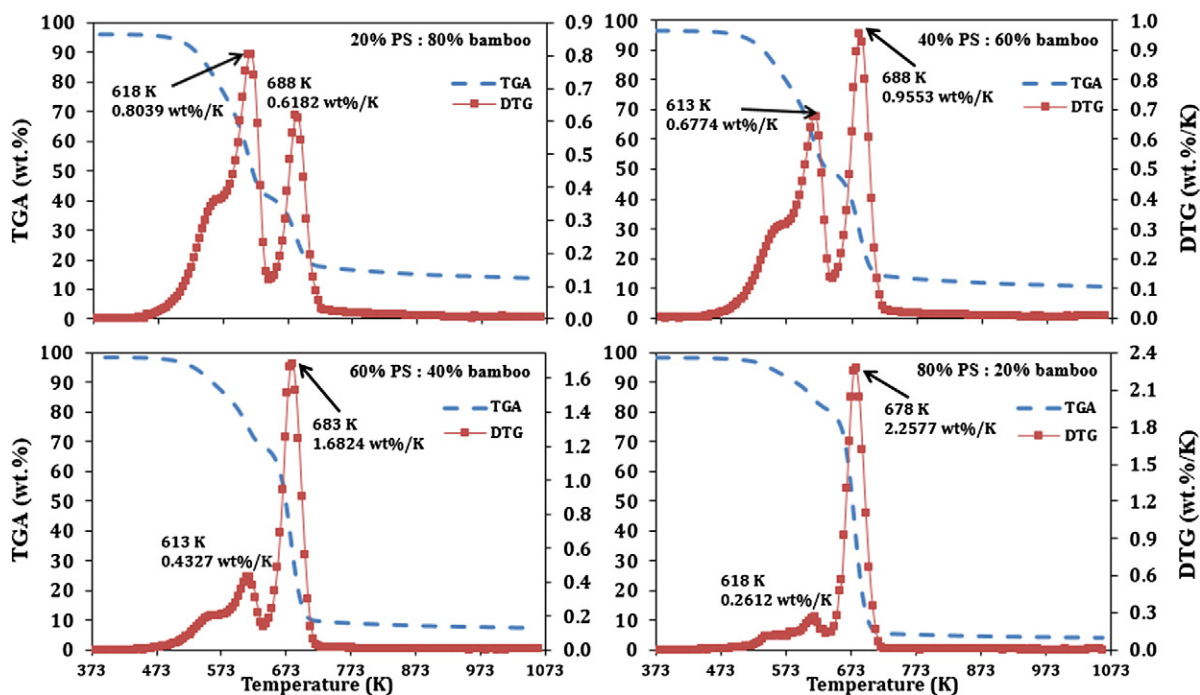


Fig. 2. TGA and DTG curves of PS and bamboo blends.

component of biomass largely decomposes at this temperature range. Therefore, the peaks exhibited at this stage are as a result of the overlap of the decomposition of biomass and plastic materials which results in increased synergic effects observed.

3.2.1. Bamboo and plastic blends

The pyrolysis distribution of the PS/bamboo and HDPE/bamboo blends at the first and second decomposition stages shows different

peak intensity depending on the blend ratios as shown in Figs. 2 and 3 respectively. The peak intensity of the first decomposition stage was only higher than the second decomposition stage when the percentage of PS and HDPE are 20%. The intensity of the second stage decomposition peak increases greatly as the plastic percentage increase from 20% to 80% in the blend while the decomposition peak for the first stage decrease accordingly. The peak intensity of the first decomposition stage at 40% bamboo was lower than that of 20% bamboo in the

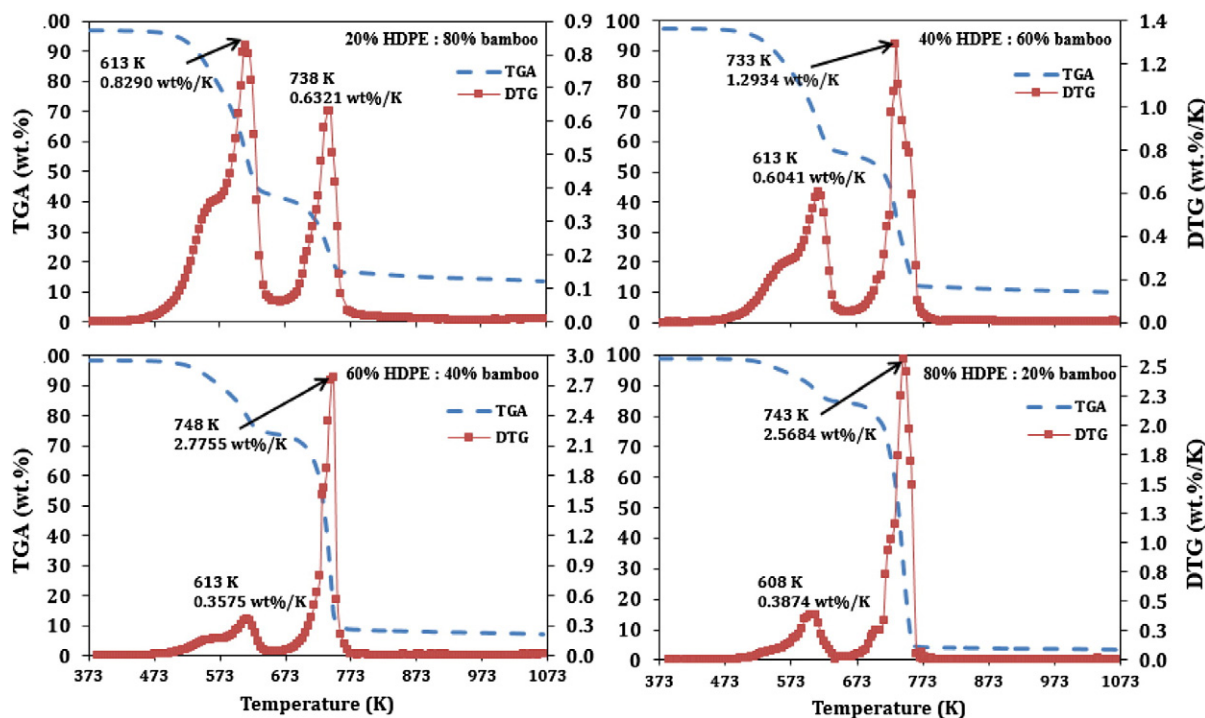


Fig. 3. TGA and DTG curves of HDPE and bamboo blends.

Table 2

Relative error calculation for experimental and calculated TGA for the HDPE/biomass co-pyrolysis blends.

Biomass sample	20% HDPE			40% HDPE			60% HDPE			80% HDPE		
	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}
Bamboo	783	7.8	5.6	738	6.1	3.9	738	23.8	5.6	743	13.7	2.5
Sawdust	758	12.5	8.1	748	22.7	11.3	728	14.1	4.6	758	22.9	12.7
EFB	748	9.6	4.2	748	13.1	5.3	753	24.7	10.4	743	18.9	9.0

* T: temperature location at the maximum relative error; Max.: maximum.

Table 3

Relative error calculation for experimental and calculated TGA for the PS/biomass co-pyrolysis blends.

Biomass sample	20% PS			40% PS			60% PS			80% PS		
	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}	*T (K)	Max. Δm_{error}	Average Δm_{error}
Bamboo	698	39.7	12.2	693	29.2	11.4	693	23.3	10.1	688	18.5	6.2
Sawdust	693	17.1	8.9	698	18.6	9.7	693	31.4	10.2	698	37.3	13.8
EFB	673	6.5	2.9	678	10.7	2.2	683	20.8	3.4	678	26.8	6.0

* T: temperature location at the maximum relative error; Max.: maximum.

HDPE/bamboo blend while the second decomposition peak intensity of 40% bamboo was higher than that of 20% bamboo. These observations were clearly different to that observed in the PS/bamboo blend.

The shoulder peak that appears to the left of the main degradation peak in Fig. 1 (biomass) was also observed in all the first decomposition peak of PS/bamboo blends as well as that of HDPE/bamboo blends.

3.2.2. Sawdust and plastic blends

The same observation that was noticed with bamboo blends was also noticed when sawdust was mixed with plastic. The second peak intensity of sawdust and PS for 60%, 40% and 20% blends are higher than that of the first peak but 80% sawdust blend with PS have a lower intensity compared to that of the first decomposition peak as shown in Appendix A.1.

In contrast, the second decomposition peak for the HDPE/sawdust blends all have higher peak intensity than the first decomposition peak compared to what was observed in HDPE/bamboo blends as demonstrated in Appendix A.2.

3.2.3. EFB and plastic blends

The pyrolysis characteristics of the EFB and plastic blends are different comparative to what was observed in the bamboo and sawdust blends with plastics as suggested by the TGA and DTG curves in Appendix A.3 and A.4 respectively. The first decomposition peak

temperature for both EFB blends was lower compared to that of bamboo and sawdust blends. This further shows that the first decomposition reaction was due to the biomass alone. The peak intensities for the second peak decompositions are all higher than the first peak decomposition intensity for PS/EFB blends with the exception of 80% EFB. In contrast, for HDPE/EFB blends, all the second peak decompositions intensities were all higher than that of the first decomposition peak intensity.

Furthermore, the first peak intensity reduces as the EFB percentage reduces for both PS and HDPE blends with the exception of 40% EFB blend where the first peak was lower than that of 20% EFB. Overall, EFB tends to have more interactions with the plastics and most especially with HDPE. The TGA and DTG curves for HDPE/EFB also showed a wide gap between the first decomposition peak and the second decomposition peaks as observed in Appendix A.4.

3.3. Interaction of plastic and biomass

The existence of interaction in the thermal decomposition of feedstock during co-pyrolysis has been subjective in the literature and also depends on the feedstocks involved in the blend. For example the results of the co-pyrolysis kinetics of coal and plastic blends by Zhou et al. [15] show significant synergic effects between coal and plastic especially at high temperature region. Also Sharma and Ghoshal [21]

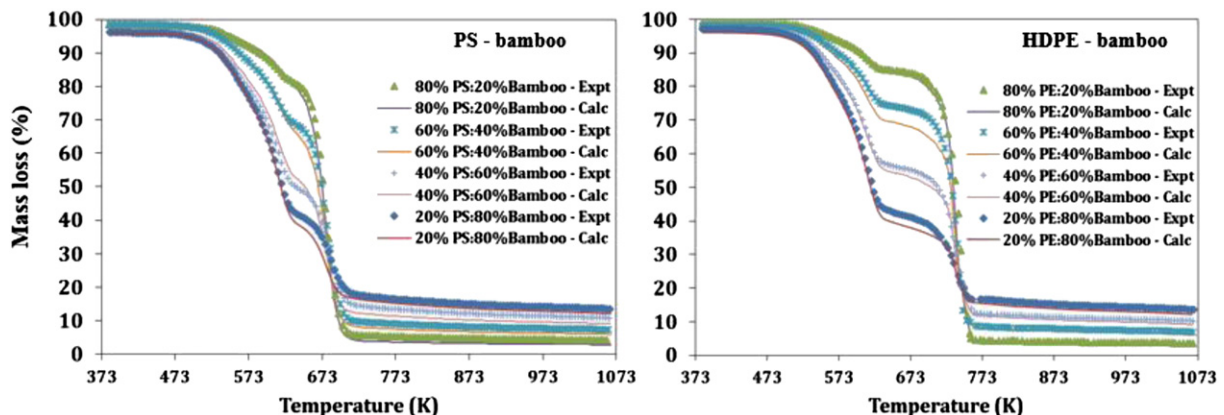


Fig. 4. Experimental and calculated TGA curves for plastic-bamboo blends.

Table 4
Kinetic parameters of the raw samples.

Sample	Temperature range (K)	Conversion (%)	E (kJ/mol)	A (min ⁻¹)	R ²
Bamboo	458–678	1–76.2	65.96	5.81 × 10 ⁴	0.9786
Sawdust	448–688	1–73.9	59.76	1.50 × 10 ⁴	0.9863
EFB	428–688	1–61.7	50.37	2.32 × 10 ³	0.9538
HDPE	663–768	1–99.2	253.69	4.60 × 10 ¹⁷	0.9739
PS	623–713	1–99.6	213.50	1.46 × 10 ¹⁶	0.9959

studied the co-pyrolysis of coal and LDPE blends and reported a deviation in the experimental data compared to the predicted ones. These results clearly show the existence of interaction between the various feedstocks in the co-pyrolysis blends.

On a contrary view, in the study by Masnadi et al. [22] on the co-pyrolysis kinetics of biomass and fossil fuels, they concluded that each feedstock reacts independently in the blend samples since no significant difference was found between the average experimental devolatilization rate and the corresponding calculated ones. Lu et al. [19] in their study on thermogravimetric study of co-pyrolysis of raw/torrefied wood and coal blends also reported slight interaction and concluded that the linear superposition of the thermal decomposition of individual fuels fits the experimental data of the fuel blends. Assuming no interaction in the thermal decomposition of plastics and biomass, the pyrolysis characteristics of the blends should follow the behavior of individual feedstock in the mixture.

In order to evaluate the possible synergic interaction between the experimental and theoretical TGA results of the plastic-biomass blends, the relative error Δm_{error} in % was calculated using Eq. (11).

$$\Delta m_{\text{error}} = \left[\frac{m_{\text{blend}} - (x_1 m_1 + x_2 m_2)}{m_{\text{blend}}} \right] \times 100 \quad (11)$$

Table 5
Kinetic parameters of the PS/biomass blends in the first and second stages.

PS content (%)	Temperature range (K)	Conversion (%)	E (kJ/mol)	A (min ⁻¹)	R ²
<i>The first decomposition – stage reaction using PS/bamboo blends</i>					
80	473–633	1–17.5	60.41	4.18 × 10 ³	0.9863
60	468–638	1–30.6	62.35	1.16 × 10 ⁴	0.9989
40	458–643	1–49.1	64.81	3.30 × 10 ⁴	0.9976
20	458–643	1–57.0	69.78	1.16 × 10 ⁵	0.9862
<i>The second decomposition – stage reaction using PS/bamboo blends</i>					
80	638–713	18.1–94.1	147.67	7.52 × 10 ¹⁰	0.9647
60	638–723	30.6–90.1	96.62	6.43 × 10 ⁶	0.9596
40	648–718	49.8–84.8	56.32	3.47 × 10 ⁴	0.9625
20%	648–713	57.5–80.9	34.06	4.30 × 10 ¹	0.9534
<i>The first decomposition – stage reaction using PS/EFB blends</i>					
80	468–613	1–14.2	61.72	8.79 × 10 ³	0.9813
60	458–603	1–22.5	62.39	2.01 × 10 ⁴	0.9895
40	448–608	1–33.3	63.12	3.47 × 10 ⁴	0.9975
20	443–608	1–46.9	63.96	6.30 × 10 ⁴	0.9870
<i>The second decomposition – stage reaction using PS/EFB blends</i>					
80	633–718	15.4–92.4	147.95	7.60 × 10 ¹⁰	0.9523
60	638–718	25.1–86.2	103.97	2.18 × 10 ⁷	0.9410
40	643–718	36.2–78.9	70.75	4.37 × 10 ⁴	0.9394
20	653–713	50.8–70.1	28.89	1.14 × 10 ¹	0.9532
<i>The first decomposition – stage reaction using PS/sawdust blends</i>					
80	488–638	1–16.9	55.65	1.52 × 10 ³	0.9978
60	463–638	1–27.5	58.54	4.67 × 10 ³	0.9899
40	463–638	1–42.7	62.34	1.78 × 10 ⁴	0.9879
20	448–643	1–57.3	63.72	3.38 × 10 ⁴	0.9965
<i>The second decomposition – stage reaction using PS/sawdust blends</i>					
80	638–728	17.3–93.5	133.48	4.74 × 10 ⁹	0.9423
60	648–713	27.5–88.9	107.75	4.95 × 10 ⁷	0.9498
40	643–713	43.3–82.6	60.35	6.86 × 10 ³	0.9520
20	653–713	58.3–77.8	28.54	1.30 × 10 ¹	0.9634

where m_{blend} is the mass loss of blend, m_i is the mass loss of each material in the same operational conditions and x_i is the weight fraction of each material in the blend.

The experimental data of the blends are compared with the calculated TG curved based on the weight percentage of each individual fuel in the blends. The results of the maximum and average relative errors as listed in Tables 2 and 3 show that good agreement was observed at the early stage of the pyrolysis below 573 K. However, during the major mass loss decomposition stage, a large lag was observed between the experimental data and the calculated data for each blend especially for PS/bamboo blends which deviated by up to 39.7% when the percentage of PS in the blend was 20%. The temperatures where the maximum relative error was located for various blends occurs at almost the same range with the exception of 20%PS 80%EFB and 20%HDPE 80% Bamboo where the temperatures at the maximum error were lower and higher than the other blends respectively.

The reason why the maximum deviation takes place at 673–698 K for PS blends and 728–783 K for HDPE blends can be attributed to the decomposition characteristics of biomass compared with plastics. Generally for biomass, decomposition starts around 473 K with cellulose and hemicellulose fraction of biomass, while degradation of lignin fraction starts above 673 K. This region overlaps with the decomposition range of plastics particularly PS. Therefore, the synergic effect has more to do with the lignin fraction of the biomass than the other component of biomass since the decomposition range of lignin and plastics is similar.

As observed in Fig. 4 at early stage below 573 K, all the calculated curves almost overlap with the experimental ones but at high temperature for the major mass loss, there exist a gap between the experimental and calculated curves. For some blend percentages, at temperatures above 773 K, the gap between the two curves was still wide apart at

Table 6
Kinetic parameters of the HDPE/biomass blends in the first and second stages.

HDPE content (%)	Temperature range (K)	Conversion (%)	E (kJ/mol)	A (min ⁻¹)	R ²
<i>The first decomposition – stage reaction using HDPE/bamboo blends</i>					
80	488–633	1–13.8	65.13	9.52 × 10 ³	0.9697
60	478–643	1–24.2	65.39	1.68 × 10 ⁴	0.9836
40	468–653	1–42.3	66.37	3.55 × 10 ⁴	0.9788
20	458–653	1–56.0	68.60	8.20 × 10 ⁴	0.9985
<i>The second decomposition – stage reaction using HDPE/bamboo blends</i>					
80	688–763	16.7–95.3	178.75	1.70 × 10 ¹²	0.9436
60	698–778	28.3–91.2	139.53	2.49 × 10 ⁹	0.9485
40	688–773	44.4–87.4	68.10	1.20 × 10 ⁴	0.9418
20%	688–758	59.0–83.8	37.89	5.62 × 10 ¹	0.9533
<i>The first decomposition – stage reaction using HDPE/EFB blends</i>					
80	473–613	1–9.3	53.73	9.60 × 10 ²	0.9719
60	453–623	1–25.2	57.00	5.44 × 10 ³	0.9788
40	448–618	1–31.8	62.58	2.90 × 10 ⁴	0.9899
20	438–618	1–45.0	64.10	5.77 × 10 ⁴	0.9935
<i>The second decomposition – stage reaction using HDPE/EFB blends</i>					
80	683–783	11.9–96.5	171.86	5.17 × 10 ¹¹	0.9488
60	673–758	28.3–86.8	93.21	9.32 × 10 ⁵	0.9428
40	688–778	37.6–82.2	70.33	1.53 × 10 ⁴	0.9532
20	698–753	50.6–75.3	67.92	1.07 × 10 ⁴	0.9495
<i>The first decomposition – stage reaction using HDPE/sawdust blends</i>					
80	478–653	1–17.9	56.21	1.53 × 10 ³	0.9788
60	458–638	1–31.9	57.07	3.79 × 10 ³	0.9944
40	463–663	1–43.0	62.27	1.40 × 10 ⁴	0.9917
20	453–658	1–55.8	63.36	2.75 × 10 ⁴	0.9899
<i>The second decomposition – stage reaction using HDPE/sawdust blends</i>					
80	693–763	21.2–93.1	163.14	1.20 × 10 ¹¹	0.9423
60	693–763	35.2–90.3	110.61	1.96 × 10 ⁷	0.9389
40	693–778	45.0–86.0	68.34	1.22 × 10 ⁴	0.9518
20	688–758	57.6–79.6	32.61	1.93 × 10 ¹	0.9423

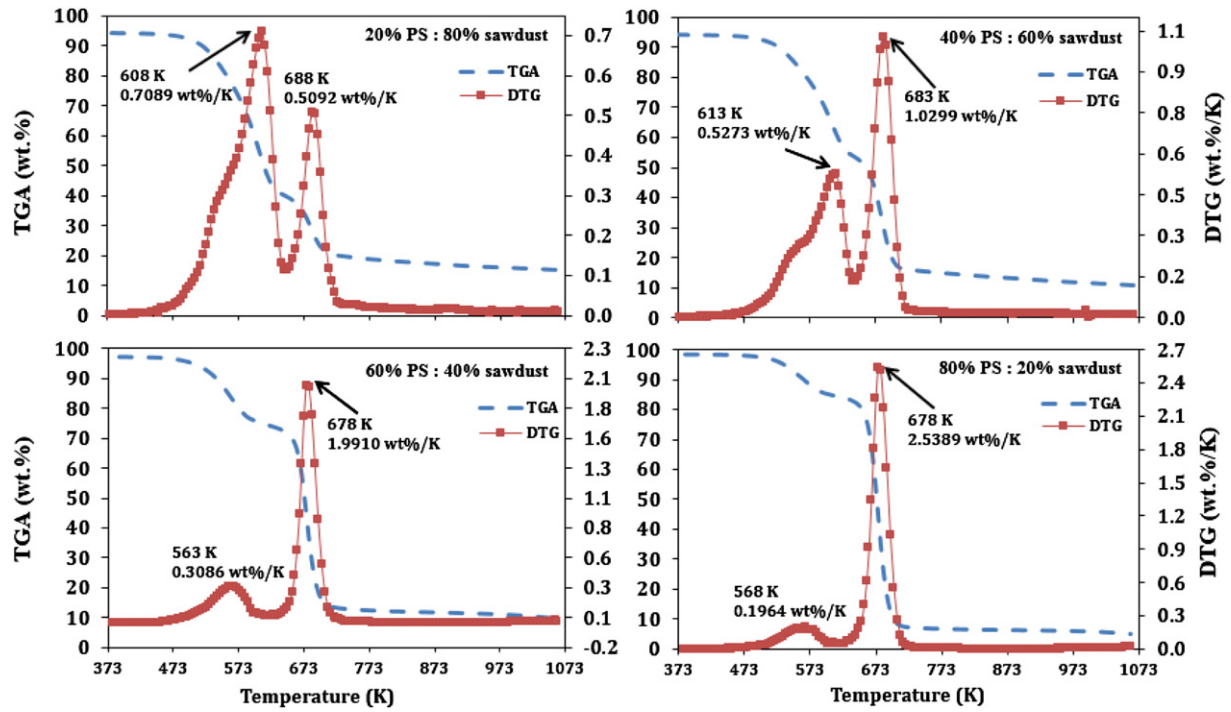


Fig. A-1. TGA and DTG curves of PS and sawdust blends.

higher temperatures. Similar observation was noticed for other biomass blends with PS and HDPE as observed in [Appendix B](#).

The detailed comparison between the experimental and calculated overall conversion for the HDPE/biomass blends and PS/biomass blends is presented in [Appendix C](#). Though it was noticed that the relative error between the experimental and calculated TGA was quite high, up to 40% for some cases, the relative error for the final overall conversion was quite low comparatively. The relative error of the overall conversion for EFB/HDPE has the highest value of 4.21% when the weight of HDPE was increased to 40%, while the relative errors for EFB/PS are all below

1%. The relative error of the final overall conversion for bamboo and sawdust for both plastic blends is below 2.4%. This shows slight difference between the experimental and the calculated overall conversion for the blends except for HDPE/EFB blends.

3.4. Kinetics analysis

The experimental data obtained from the TG analysis were used to calculate the kinetic parameters concentrating only on the main degradation region for each material and blends. The pre-exponential factors,

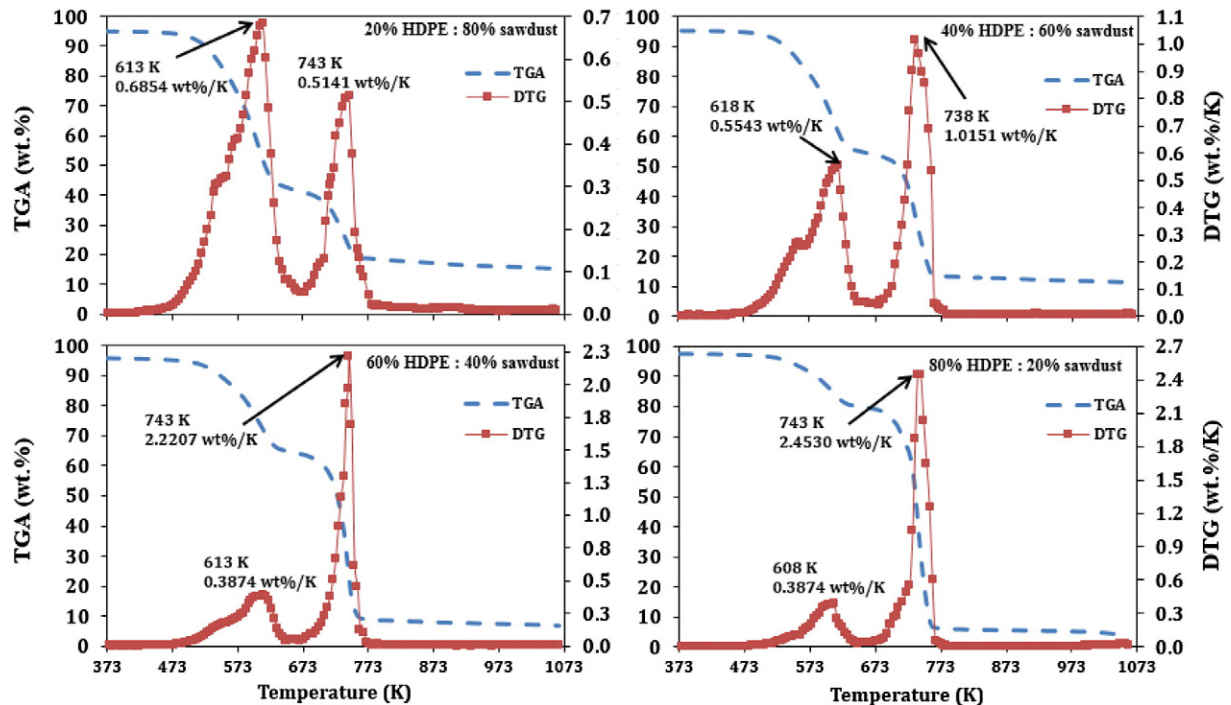


Fig. A-2. TGA and DTG curves of HDPE and sawdust blends.

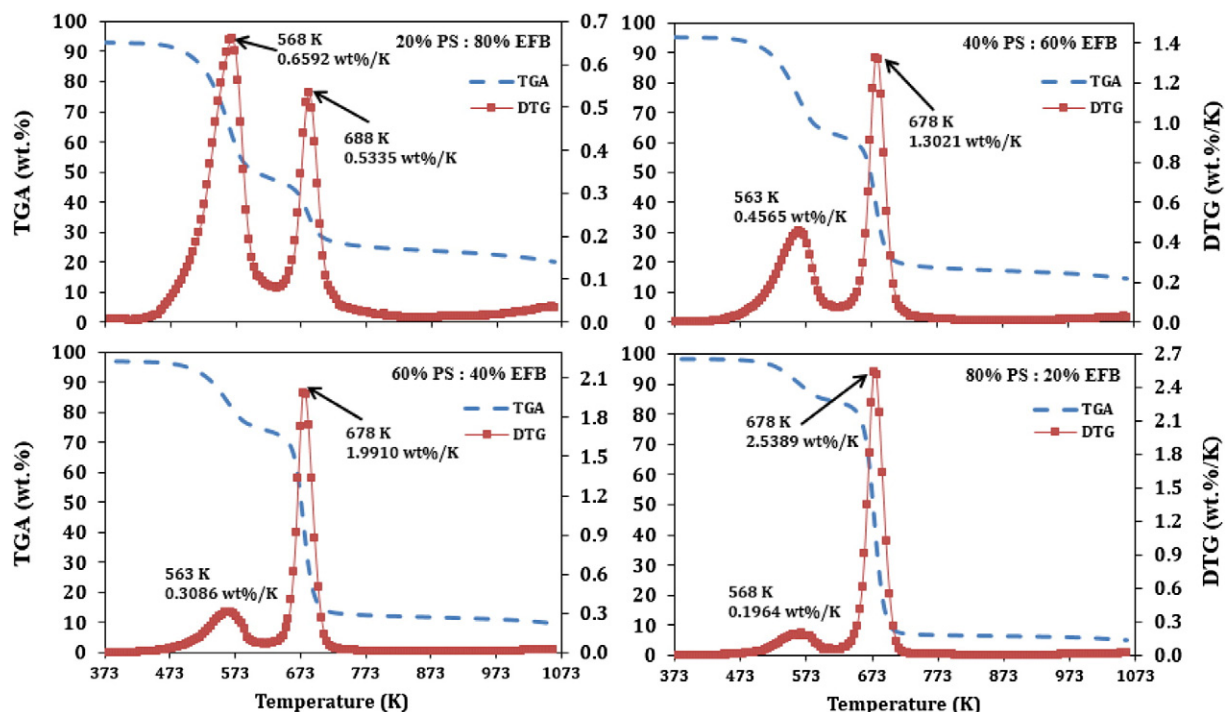


Fig. A-3. TGA and DTG curves of PS and EFB blends.

activation energies and the conversion range of the raw materials, the PS/biomass blends and the HDPE/biomass blends are presented in Tables 4, 5 and 6 respectively. It was assumed that the pyrolysis thermal decomposition reaction is a first order reaction and we also assume a single step reaction for each individual feedstock and two step reactions for all blends. The corresponding values of R^2 are all more than 0.94, reflecting that the pyrolysis analysis and kinetics were well correlated. The kinetic parameters are further discussed respectively.

3.4.1. Kinetic parameters of materials

The kinetic parameters of the materials as presented in Table 4 show that bamboo has the highest conversion among the biomass materials with E value of 65.96 kJ/mol followed by sawdust and EFB. When considering the plastic materials, HDPE was more reactive than PS with higher E value of 253.69 kJ/mol and higher pre-exponential factors. The result also confirms that biomass decompose at lower temperature <688 K, while plastics decompose at a higher temperature range. HDPE

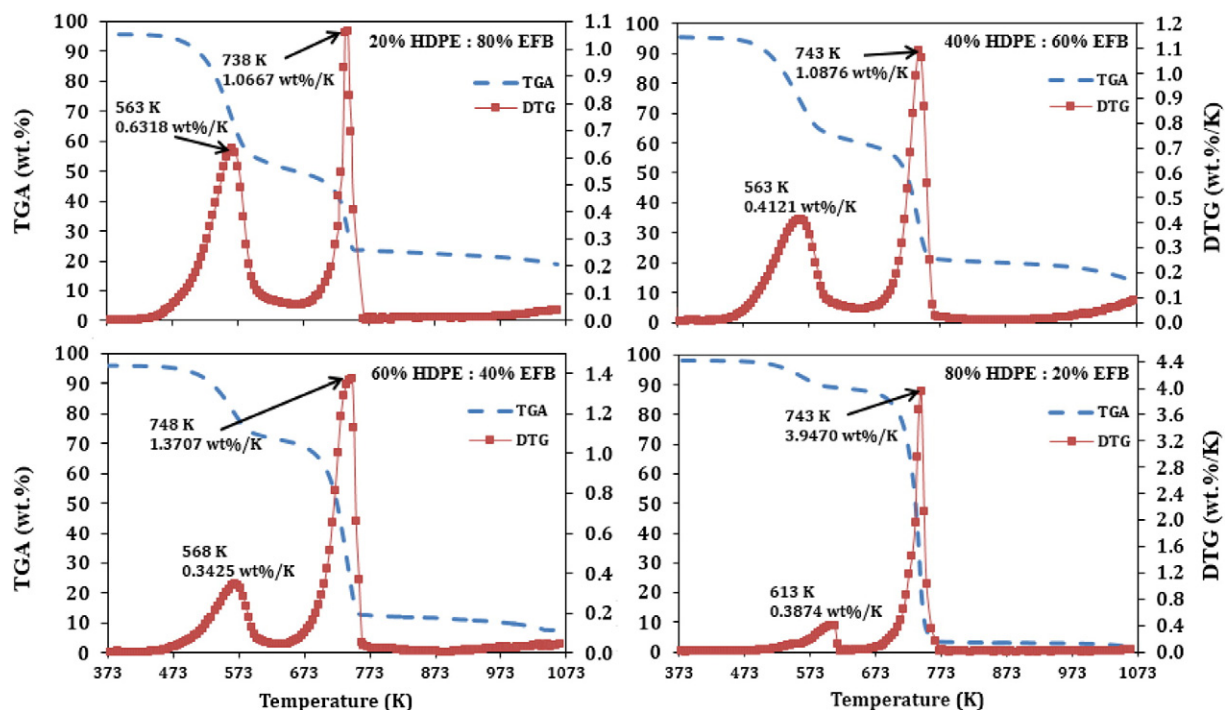


Fig. A-4. TGA and DTG curves of HDPE and EFB blends.

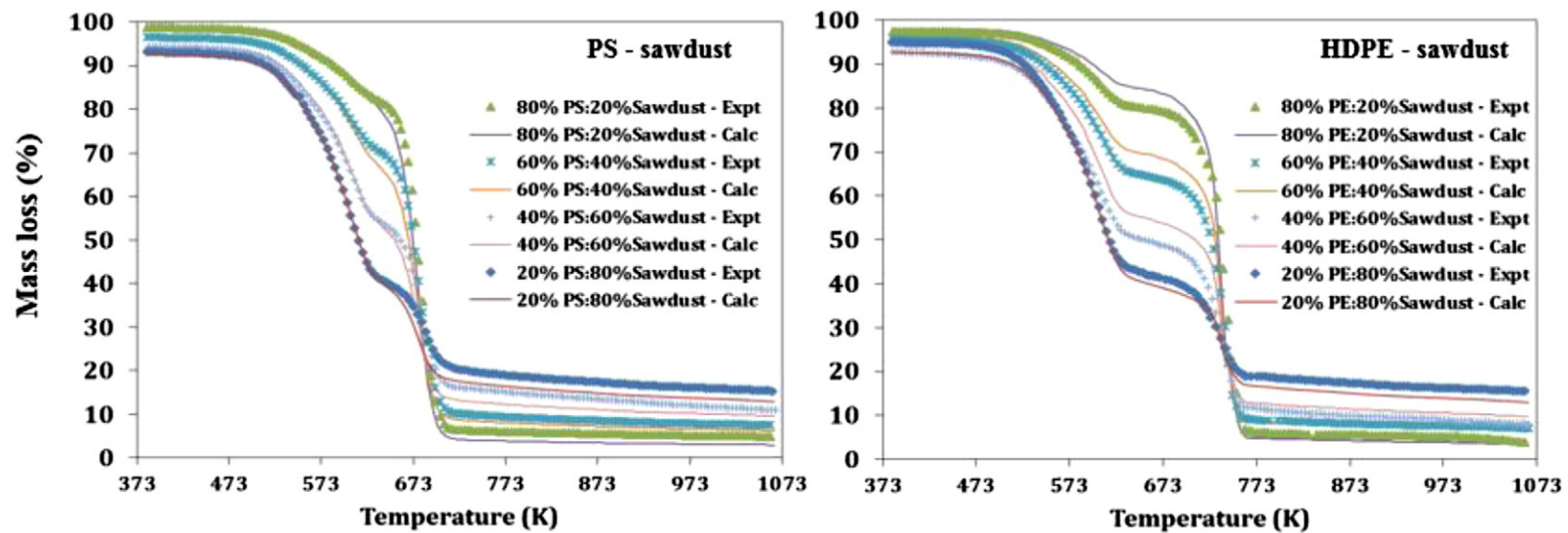


Fig. B-1. Experimental and calculated TGA curves of plastic-sawdust blends.

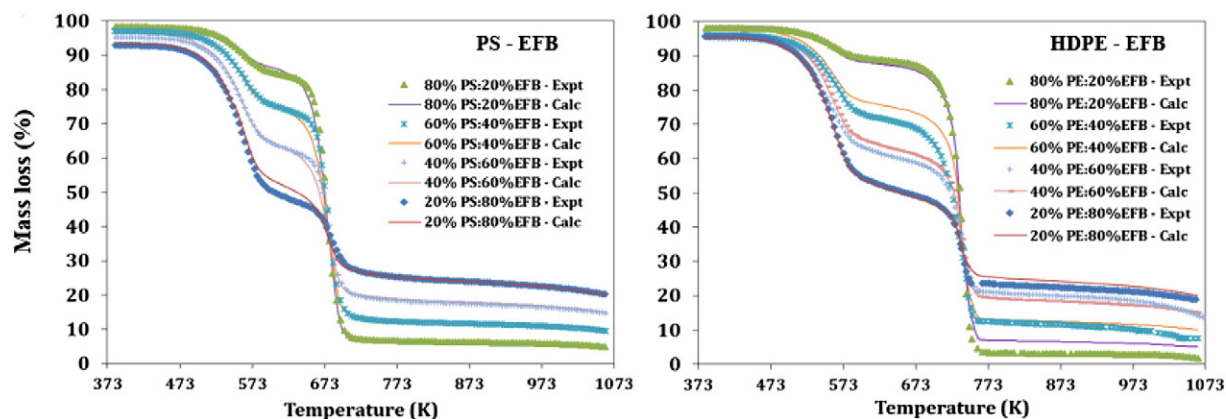


Fig. B-2. Experimental and calculated TGA curves of plastic-EFB blends.

decompose around 663–768 K, while the range of decomposition of PS is 623–713 K. The kinetic parameters obtained for the plastic materials are similar to that obtained by Encinar and Gonzalez [23].

3.4.2. Kinetic parameters of blends

The results of the kinetic parameters as observed in Tables 5 and 6 show that the weight percentage of plastics in the mixture has more influence on the obtained parameters. When the weight percentage of PS or HDPE in the mixture decreases, the values of the pre-exponential factor and activation energy in the first stage have an increasing trend but cause a decreasing trend in the second stage decomposition reaction. The rate of increase in activation energy as the weight percentage of PS or HDPE decreases in the first stage decomposition was very low compared to the rate of reduction in the activation energy for the second stage decomposition reaction. HDPE/EFB was very reactive with higher activation energy and pre-exponential factor at 80% EFB for second decomposition reaction compared to 80% of other biomass materials in the HDPE blends.

Comparing the calculated kinetics parameters of the blends in Table 5 and 6, it can be clearly seen that the temperature and energy needed for the decomposition of HDPE/biomass blends is higher than that of the PS/biomass blends. The results also show that plastic/biomass blends have different pyrolysis reactivities at different temperature ranges with varying activation energies. The good correlation coefficient indicates that the corresponding independent first-order reaction model fits the experimental data very well.

4. Conclusion

In this study, we have examined the thermogravimetric and kinetic study of the co-pyrolysis of biomass and plastic blends. The result shows that the thermal decomposition of the materials can be characterized by one single reaction stage, while that of the blends can be characterized by two decomposition reaction stages.

The results of the analyses suggested that the co-pyrolysis characteristics of the blends are quite different to the combination of the individual materials and therefore it can be concluded that there exist interactions and significant synergic effects between

plastic and biomass co-pyrolysis. Our results shows that the synergic effect was influenced by the plastic composition as up to 25% deviation was observed between the experimental and calculated TGA for HDPE/biomass blends and up to 40% deviation was observed for PS/biomass blends. It was also noticed that despite the high relative errors between the experimental and calculated TGA curves for the blends, the relative error for the final overall conversion was minimal.

The examination of the kinetic of the blends indicates that an increase in plastic percentage in the blends leads to decrease of activation energy for the first decomposition stage reaction and subsequently increases the activation energy for the second decomposition stage reaction. Overall, the results show that plastic/biomass blends have different pyrolysis reactivities at different temperature ranges with higher temperature and energy needed for the decomposition of HDPE/biomass blends than the PS/biomass blends.

Nomenclature

A	pre-exponential factor, min^{-1}
α	conversion of sample
β	heating rate, K/min
E	activation energy, kJ mol^{-1}
k	kinetic rate constant
m	weight of sample, mg
n	order of reaction
R	universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
t	heating time, min
T	temperature, K
x_i	the weight fraction of each material in the co-pyrolysis blends.
Δm_{error}	relative error, %

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Table C-1

A comparison of overall conversion at 1073 K between the experimental and calculated TGA for the HDPE/biomass co-pyrolysis blends.

Biomass sample	20% HDPE			40% HDPE			60% HDPE			80% HDPE		
	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}
Bamboo	86.0	87.1	1.4	89.5	90.3	1.2	93.0	93.4	0.5	96.4	96.6	0.2
Sawdust	83.7	85.7	2.4	88.2	89.3	1.3	92.6	92.7	0.1	96.0	96.2	0.3
EFB	80.3	78.7	2.1	87.6	83.9	4.2	92.1	89.2	3.2	96.5	94.4	2.2

Expt.: experiment; Calc.: calculation; Δm_{error} : relative error.

Table C-2

A comparison of overall conversion at 1073 K between the experimental and calculated TGA for the PS/biomass co-pyrolysis blends.

Biomass sample	20% PS			40% PS			60% PS			80% PS		
	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}	Expt.	Calc.	Δm_{error}
Bamboo	85.9	87.2	1.5	88.8	90.4	1.8	92.5	93.6	1.2	95.7	96.8	1.1
Sawdust	83.8	85.8	2.4	88.4	89.3	1.1	92.1	92.9	0.8	95.0	96.4	1.6
EFB	78.2	78.7	0.6	84.5	84.0	0.5	90.1	89.4	0.8	94.9	94.7	0.3

Expt.: experiment; Calc.: calculation; Δm_{error} : relative error.

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Appendix A. Pyrolysis characteristics of co-pyrolysis blends

Appendix A.1. Sawdust and PS blends

The TGA and DTG curves of the blends of sawdust and PS are shown in Fig. A-1.

Appendix A.2. Sawdust and HDPE blends

The TGA and DTG curves of the blends of sawdust and HDPE are shown in Fig. A-2.

Appendix A.3. EFB and PS blends

The TGA and DTG curves of the blends of EFB and PS are shown in Fig. A-3.

Appendix A.4. EFB and HDPE blends

The TGA and DTG curves of the blends of EFB and HDPE are shown in Fig. A-4.

Appendix B. Comparisons of experimental and calculated TGA curves of biomass/plastic blends

Appendix B.1. Sawdust and plastic blends

The experimental and calculated TGA curves of the blends of sawdust and plastics are shown in Fig. B-1.

Appendix B.2. EFB and plastic blends

The experimental and calculated TGA curves of the blends of EFB and plastics are shown in Fig. B-2.

Appendix C. Comparisons of overall conversion at 1073 K between the experimental and calculated TGA for plastic/biomass blends

The overall conversion (%) of raw bamboo, sawdust, EFB, PS and HDPE at 1073 K are 84, 82.2, 73.4, 100 and 99.7 respectively. The overall conversion of the biomass improved as the percentage of plastics increases as shown in Table C-1 and C-2.

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